Assessing the Oxidative Capacity of the Atmosphere: MCMA-2003 as a Case Study

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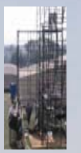
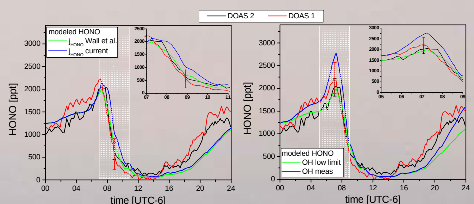
Abstract:
Measurements from the Mexico City Metropolitan Area (MCMA) field campaign in 2003 (MCMA-2003) and a photochemical box model employing the Master Chemical Mechanism (MCMv3.1) are used to study primary HO_x (=OH+HO_2) radical sources and RO_x radical cycling. HONO measurements are accurately modeled using an equilibrium model constrained for OH, NO, and photolysis. A source apportionment of photochemical HCHO is performed considering: VOC precursors, oxidants, and primary vs. secondary oxidation. The box model is used to assess the level of constraint on primary radical sources (due to gas-phase processes). Predicted concentrations of HO_x, when compared to measurements, demonstrate a significant lack of HO_2 radicals in the early morning: This "missing reactivity" is highest during peak photochemical activity and has a significant impact on both VOC oxidation and ozone production throughout the day.



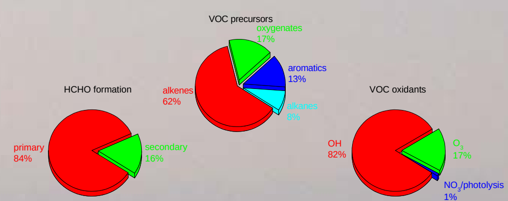
Measurements from MCMA-2003 (CENICA):
- primary radical sources: HONO, HCHO, O_3, alkenes/O_3[1,2]
- radical sinks: 103 VOC (55 VOC by measurements[2,3]), NO, NO_2, SO_2, CO
- temperature, pressure, dilution[4], j-values[1]
- OH and HO_2 measurements; also OH reactivity/loss[5]

Model description:
- steady-state, flexible-top, photochemical box model
- Master Chemical Mechanism (MCMv3.1[6,7]):
  - near-explicit mechanism (135 VOC, 13500+ reactions); ideal for RO_x radical modeling; no chemical lumping
- modeling scenarios: HO_x-unconstrained, OH-constrained, HO_2-constrained, HO_x-constrained

Radical sources: HONO and HCHO

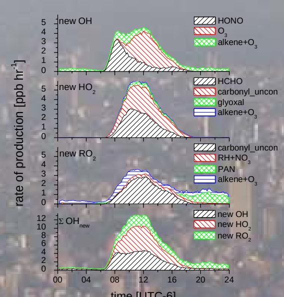


A **lower limit of measured OH** – based on a 0.01 pptv statistical offset – and a new recommendation[8] for **j(HONO)** bring measured and modeled values into agreement; HONO is accurately predicted with an equilibrium model (commonly referred to as photostationary state, PSS; we do not use this term because we use night-time OH values)

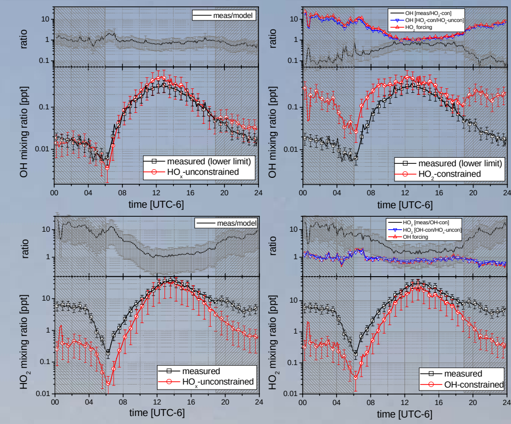


Up to 70% of the observed HCHO is produced from photochemistry[9]: The bulk of **photochemical HCHO** produced in the MCMA is from the **primary** oxidation of **alkenes**; **OH** is the dominant oxidant, while $\mathbf{O_3}$ makes a minor contribution.

The photolysis of HONO, O_3, and HCHO, and O_3/alkene reactions account for some 60% of the primary HO_x flux on average; even though unconstrained carbonyls – formed as secondary oxidation products – contribute up to 40% of new RO_x, the model is well-constrained for gas-phase primary radical sources.



% contribution to ΣOH_{new}	03:00	07:00	08:00	09:00	11:00	13:00	15:00	06-18 (avg)
HONO	--	50.2	44.9	26.1	8.2	5.1	5.7	15.6
O_3	--	0.1	0.5	4.0	20.5	29.2	20.1	13.0
HCHO	--	5.5	10.4	20.6	21.5	17.7	13.3	13.7
CHOCHO	--	0.2	0.5	1.2	2.7	3.2	2.9	1.9
alkenes + O_3	95.0	24.7	21.8	20.2	8.8	5.7	11.0	18.1
→OH	*48.3*	*11.9*	*10.7*	*10.2*	*4.6*	*3.0*	*5.3*	*8.9*
→HO_2	*7.1*	*1.6*	*1.6*	*1.7*	*1.0*	*0.7*	*1.2*	*1.6*
→RO_2	*39.6*	*11.2*	*9.5*	*8.3*	*3.2*	*2.0*	*4.5*	*7.6*
carbonyls	--	18.1	21.4	26.2	35.2	35.0	41.1	30.1
→HO_2	--	*9.1*	*11.0*	*14.0*	*20.0*	*20.2*	*21.6*	*16.4*
→RO_2	--	*9.0*	*10.4*	*12.2*	*15.2*	*14.8*	*19.5*	*13.7*
RH + NO_3	5.0	0.2	0.3	1.0	1.8	2.3	4.2	3.2
sum	100	99.0	99.8	99.3	98.7	98.2	98.3	95.6



- Model accurately predicts HO_x diurnal profiles; with the exception of the prediction of OH in the HO_2-constrained case; predicted OH is within measured and modeled uncertainties for the entire day
- HO_2 is consistently under-predicted at night and in the morning (06-08:00) in both the HO_x-unconstrained and OH-constrained scenarios
- The model is missing a HO_2 source; however, the source cannot generate OH via cycling
- HO_2-constrained model drastically over-predicts OH

What does this mean in terms of VOC oxidation and ozone formation?

Relevant definitions/descriptions:
1) chain length: number of times that OH will be regenerated via RO_x cycle before it is removed
2) HO_2/OH v NO and **3)RO_2/HO_2 v NO**: key ratios to test our understanding of RO_x cycling
4) ozone production rate, $P(O_3)$: expressed here as number of NO-to-NO_2 conversions from RO_x radicals

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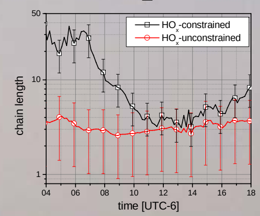

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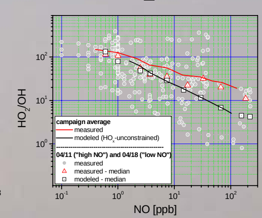

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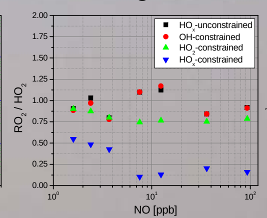

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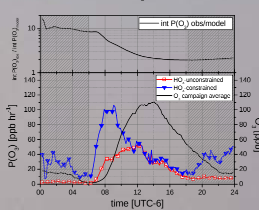

Key findings:
1) chain length: drastic under-prediction of OH cycling in the early morning hours (06:00-08:00) in the HO_x-unconstrained case, a difference of a factor of 2 - 9.
2) HO_2/OH v NO: a) at high NO (in the morning) the ratio is a factor of 3 smaller than the measured ratio, and overall, the measured and modeled slopes vary significantly. b) modeling of individual days ("high NO" and "low NO" day) demonstrates that conclusions based on a campaign averaged model are appropriate.
3) RO_2/HO_2 v NO: note the low ratio in the HO_x-constrained case (red circles), especially at high NO; the coupling between OH and RO_2 yields a lower-than-expected RO_2/HO_2 ratio.
4) $P(O_3)$: in the early morning, the greatest percentage of NO-to-NO_2 conversions take place, with the lack of predicted radicals resulting in a factor of 10 difference in cumulative ozone production in the predicted vs observed cases. In the mid-afternoon (16:00), the model underestimates cumulative ozone production by 70%.

Conclusions:
\+ Recommended lower limit for night-time and morning OH; confirmation of updated j(HONO) value
\+ An equilibrium model – with HONO sources and sinks constrained – accurately predicts measured HONO concentrations throughout the day
\+ Primary radical sources are well-constrained by measurements; HCHO is the predominant day-time HO_x radical source
\+ We accurately predict OH; however, we drastically under-predict HO_2 at night and in the early morning, which has significant implications for O_3 formation throughout the day; we are missing an HO_2 source

References: [1]Volkamer et al, GRL,32 (2005); [2]Velasco et al, ACPD,7563 (2006); [3]Volkamer et al, Atmos Env,3731 (1998); [4]de Foy, Garcia, personal communication; [5]Shirley et al, ACP,3163 (2006); [6]Bloss et al, ACP,623 (2005); [7]Bloss et al, ACP,641 (2005); [8]Wall et al, J Atmos Chem, 31 (2006); [9]Garcia et al, ACPD,11583(2005)

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